

LOW TEMPERATURE METHANE PRODUCTION BY THE CATALYZED REACTION OF
GRAPHITE AND WATER VAPOR

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The gasification of carbon (coal) by reaction with water vapor is usually conducted at a temperature higher than 1200K. This reaction exhibits an apparent activation energy of the order of 50 kcal/mole. It is catalyzed by various salts of alkali metals, especially potassium [1,2]. At these high temperatures, the main products are CO and H₂, according to the reaction



The simultaneous production of CH₄ has also been reported [3] especially when the reaction temperature is lowered. The relatively high temperature would, however, facilitate the decomposition of most hydrocarbons that could have been produced.

Our research is focussed on finding suitable catalysts for the low temperature production of low molecular weight hydrocarbons from the reaction of carbon (coal) with water vapor. It has been reported recently that potassium hydroxide, potassium carbonate and several other alkali metal hydroxides catalyze the production of methane in the temperature range from 500 to 600K with an apparent activation energy of about 11 kcal/mole [4]. In order to gain more insight into the mechanism of this production, this study has been extended by

- i) using two different reactors to accomodate either graphite single crystals or graphite powder,
- ii) extending the temperature range up to 1075K,
- iii) varying of the reactor vapor pressure, and
- iv) investigating other catalysts: calcium oxide and transition metals.

Graphite single crystals were obtained by cleavage from a larger piece of highly oriented pyrolytic graphite (HOPG) from Union Carbide Corporation. They were mounted on the manipulator of a UHV system, in firm contact with a gold foil that could be heated resistively. The sample was accessible to surface analysis by AES, XPS, ion sputter cleaning and mass spectrometry. It could also be isolated within a high pressure cell where it was exposed to water vapor and/or other gases for chemical reaction. The products were analyzed by gas chromatography. This apparatus has been described in more detail elsewhere [4].

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Pure graphite powders were reacted with water in a fixed bed reactor made of a quartz tube 4 min. ID containing about 0.4 g of sample fixed between two glass wool plugs. A carrier gas (usually nitrogen) was saturated with water vapor by bubbling through a water container where the temperature could be adjusted from 30°C to 95°C in order to vary the water vapor pressure. The flow rate could be varied between 4 and 20 ml/min. At the outlet of the reactor, the water vapor was condensed in a copper coil maintained at the melting ice temperature. Care was taken to avoid the condensation of water in other parts of the apparatus. The products were analyzed by gas chromatography.

The potassium hydroxide catalyzed reaction was studied from 525 to 1075K under a water vapor pressure ranging from 20 to 600 torr. The production of methane exhibited the same apparent activation energy of about 12 kcal/mole within the whole temperature range. This suggests that the catalytic mechanism involved remains the same at high temperature and has no relation to the (simultaneously occurring) reaction (1). The methane production appeared also to be first order with respect to the water vapor pressure.

Calcium oxide was also tried as catalyst in the temperature range 623-873K [5]. Single crystal graphite samples were impregnated with 1M solution of $\text{Ca}(\text{NO}_3)_2$ and dried in air. CaO was obtained from the decomposition of $\text{Ca}(\text{NO}_3)_2$ at the temperature of the reaction. No methane was detected when the sample was exposed only to 22 torr of H_2O and 730 torr of helium. XPS analysis showed, however, the appearance of a new peak at a binding energy of 290 eV. Methane was readily detected when the sample was subsequently exposed to 1 atm H_2 at the same temperature. The intensity of the peak at 290 eV decreased simultaneously with increasing time of reaction with hydrogen. We tentatively attribute this peak to a new form of active carbon that is hydrogenated to CH_4 by H_2 . A steady rate of production of methane was obtained when reacting the sample in a mixture of 22 torr of H_2O and 32 torr of H_2 . This reaction had an apparent activation energy of 16.3 kcal/mole and exhibited a first order dependence on the hydrogen pressure.

Alkali and calcium catalysts do not produce organic molecules other than methane under our experimental conditions. Studies are now in progress to determine if the combination of these catalysts with transition metal compounds could be utilized to produce higher molecular weight hydrocarbons.

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